



Naval Fuels & Lubricants

Cross Functional Team

Research Report

50/50 F-76/DSH-76 SPECIFICATION AND FIT-FOR-PURPOSE LEVEL I TEST RESULTS

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EXECUTIVE SUMMARY

Direct sugar to hydrocarbon diesel (DSH-76) is an iso-paraffinic single molecule fuel produced from direct fermentation of renewable sugars. This test report summarizes chemical, physical and fit for purpose (FFP) test results of a 70/30 and 50/50 blend of petroleum F-76 and DSH-76. The 70/30 and 50/50 F76/DSH-76 met all specification properties as set forth by MIL-DTL-16884L and FFP criteria as set forth by NAVSEA technical warrant holders, engine OEMs and subject matter experts¹. Chemical profiling showed the chemical composition of neat DSH-76 to consist of a C15 iso-paraffinic molecule with very little side products. These test results support the continued qualification of 50/50 F76/DSH-76 for shipboard use by the U.S. Navy.

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50/50 F-76/DSH-76 SPECIFICATION AND FIT-FOR-PURPOSE LEVEL I TEST RESULTS

1.0 BACKGROUND

In October 2009, Secretary of the Navy Ray Mabus directed the Navy to decrease its reliance on fossil fuels. The Secretary set a goal of operating with at least 50% of Navy energy consumption coming from alternative sources by 2020. He also set forth the goal of demonstrating a Great Green Fleet, operating on 50% alternative fuel, by 2012 and deploying in 2016. The use of 50%/50% alternative/petroleum sourced aviation and marine diesel fuels is a critical component to achieving these goals. The alternative sourced fuels will come from non-food sources and must be compatible with all existing hardware without compromising performance, handling or safety. The increased use of alternative sources to produce Navy tactical fuels will increase the Navy's energy independence while improving national security, decreasing environmental impact and strengthening the national economy. The objective of this test program is to ensure that all proposed alternative fuels perform equally or greater than existing petroleum sourced fuels. Specification and fit-for-purpose testing are the first two steps in the Navy's qualification program.

2.0 APPROACH

The overarching approach of the Navy's alternative fuels qualification program is to ensure that proposed fuels perform similar to or better than equivalent petroleum fuels. The initial evaluations have focused on a F-76 produced from a blend of alternative sources and petroleum. The qualification testing conducted in accordance with Navy Standard Work Package 44FL-005 (Naval Fuels and Lubricants CFT Shipboard Propulsion Fuel, F-76, Qualification Protocol for Alternative Fuel/ Fuel Sources) includes specification, fit-for-purpose, critical component testing, engine testing, and full scale demonstrations with decision points built in after each stage is completed. In general, the testing program progresses from the low risk, low cost, low fuel consumption, and least complex testing to the greatest of each of these categories. This report discusses the results of specification and fit-for-purpose level I testing. Follow on reports will be issued as component testing, engine testing, and full scale demonstrations are completed.

2.1 Fuels

An alternative sourced diesel fuel under-going qualification testing is a blend of direct sugar to hydrocarbon diesel fuel (DSH) with petroleum F-76. DSH fuels are made from direct fermentation of sugar into olefinic hydrocarbons. The olefinic hydrocarbons are hydroprocessed to produce an iso-paraffinic hydrocarbon. To represent this class of renewable diesel fuel, DLA Energy contracted on behalf of the Navy to procure DSH-76 that was a 98% pure branched

paraffin with a fifteen carbon chain called 2,6,10 trimethyldodecane or farnesane. This fuel was unique because it was a single molecule; unlike petroleum fuels or Hydroprocessed Renewable Diesel (HRD-76) that have a broad range of different normal and iso paraffins. The impact to fuel properties of a single molecule fuel and potential impact to engine performance will be discussed in this report.

Two distinct batches of DSH-76 were evaluated for this report. Batch 1 was defined as the 165 gallons received on February 9, 2012 and was provided for a preliminary chemical evaluation prior to larger scale procurement. Batch 2 was the 5,000 gallon procurement received on January 16, 2013 and was procured by DLA for engine component testing, full scale engine testing, and platform trials. Batch 1 of DSH-76 was blended 50%/50% and 70%/30% (by volume) with petroleum F-76. These blends from Batch 1 are herein referred to as blend 1 and blend 2 respectively. Batch 2 was blended 50%/50% (by volume) with petroleum F-76 and is herein referred to as blend 3.

2.2 Specification Testing

The DSH-76 procurement specification describes requirements neat DSH-76 must meet at the time of delivery to the Navy. The procurement specifications for neat DSH-76 are provided in Appendix A.

Naval distillate fuel (diesel), F-76, is governed by MIL-DTL-16884. 70/30 and 50/50 F76/DSH-76 must meet all requirements of MIL-DTL-16884 in order to continue qualification. The most recent version of the military specifications can be found at <http://quicksearch.dla.mil/>.

2.3 Fit-for-Purpose Testing

Fit-for-purpose (FFP) properties are chemical and physical properties of a fuel that are not typically measured for petroleum derived fuels because they are inherently acceptable. These properties impact the performance, materials compatibility, handling, and safety of the fuel and therefore must be evaluated for any non-petroleum fuel. The FFP properties were chosen through consultations with original equipment manufacturers (OEM) and Navy subject matter experts (SMEs) as those that could reveal effects to their relevant equipment. The purpose of testing FFP properties is to ensure that there are no unintentional consequences to changing the source of the fuel. The FFP properties are split into two levels. Level I properties can be tested using small amounts of fuel (typically 5 gallons) while Level II tests generally require larger fuel volumes (approximately 800 gallons), are more complex, and typically require longer schedule lead times. This report provides the Level I results. Additional information about the FFP selection criteria, parameters and limits can be found in Reference 1.

3.0 RESULTS & DISCUSSION

3.1 Direct Sugar to Hydrocarbon F-76 (DSH-76) Procurement Specification Test Results

The neat finished fuel must meet DSH-76 marine diesel procurement specification requirements before consideration for the fuels evaluation process. These requirements are found in Appendix A. DSH-76 procurement specification data for both batches is displayed in Table 1. Batch 2 met

all the DSH-76 procurement requirements, but Batch 1 did not meet the total alkali metals procurement requirement due to a high silicon concentration. The high silicon concentration of Batch 1 may have been due to external contamination and not inherent to the production of DSH. This was affirmed by the lack of silicon in Batch 2. Physical and chemical properties of each batch are consistent.

Table 1. DSH-76 Procurement Specification Data for Neat DSH-76 Batches 1-2

Test	Parameter	Method	Units	Minimum	Maximum	DSH-76 Batch 1	DSH-76 Batch 2
Flash Point		D93	°C	60		85	106
Density at 15°C		D4052	kg/L	0.772	0.800	0.773	0.777
Total Water		D6304	ppm		200	NR	NR
Particulate Contamination		D6217	mg/L		1.0	0.0	0.1
Viscosity at 40°C		D445	cs	1.7	4.3	2.3	2.4
Cetane Number, Derived		D6890	----	42	80	60	58
Cetane Index		D976	----	43	80	71	71
Distillation	Initial Point	D86	°C	Report		238	236
	10% Recovered	D86	°C	191	290	244	242
	50% Recovered	D86	°C	Report		244	245
	90 % Recovered	D86	°C	230	357	245	245
	End Point	D86	°C	235	385	255	258
	Residue	D86	Volume %			1	2
	Loss	D86	Volume %			0	0
	Residue + Loss	D86	Volume %		3.0	1.3	1.6
	T50 - T10		°C	Report		0	2
	T90 - T10		°C	Report		1	3
Carbon Residue on 10% Bottoms		D524	Mass %		0.20	0.0	0.0
Copper Strip Corrosion at 100 °C		D130	----		1	1a	1a
Cloud Point		D5773	°C		-1	-81	-82
Hydrogen Content		D7171	Mass %	13.0		14.9	14.8
Heating Value		D4809	MJ/kg	43.0		43.9	43.8
MSEP Diesel Capsule		D7261	----	85		NR	NR
Acid Number		D974	mgKOH/g		0.08	0.01	0.01
Additives	Antioxidant A		ppm			NR	14.9
	Antioxidant B		ppm			NR	0.0
	Antioxidant C		ppm			NR	6.2
	Total Antioxidant		ppm	17.2	24.0	NR	21.1
Sulfur, Total	XRF or,	D4294	Mass %		0.0015	N/A	0.0001
	UV Fluorescence	D5453	ppm		15	0	1
Nitrogen Content		D4629	ppm		10	2	1
Metals	Ca	D7111	ppm			< 0.1	<0.001
	Cu	D7111	ppm			< 0.1	<0.01
	Fe	D7111	ppm			< 0.1	0.0
	Mg	D7111	ppm			< 0.1	<0.002
	Mn	D7111	ppm			< 0.1	0.0
	Ni	D7111	ppm			< 0.1	<0.07
	P	D7111	ppm			< 0.1	<0.09
	Pb	D7111	ppm			< 0.1	<0.01
	V	D7111	ppm			< 0.1	<0.01
	Zn	D7111	ppm			< 0.1	0.0
	Total Metals	D7111	ppm		0.5	< 0.1	0.0
Alkali Metals & Metalloids	B	D7111	ppm			0.0	0.1
	Na	D7111	ppm			0.2	<0.16
	K	D7111	ppm			0.1	0.1
	Si	D7111	ppm			1.3	0.2
	Li	D7111	ppm			< 0.1	0.0
	Total	D7111	ppm		1.0	1.6	0.0

*Values highlighted in red denote properties that do not meet procurement specification

3.2 MIL-DTL-16884L- F-76 Specification Test Results

70/30 and 50/50 F-76/DSH-76 fuels were evaluated for specification properties according to MIL-DTL-16884L. Specification properties of the base petroleum fuel and the unblended DSH-76 were also tested for comparison purposes. Results for Batches 1 and 2 are summarized in Tables 2 and 3 respectively. In all cases the neat DSH-76, F-76/DSH-76 fuel blends, and neat petroleum F-76 met or exceeded the specification requirements. Properties of the neat DSH-76 such as flash point, density, pour point, carbon residue, hydrogen content and ignition quality often exceeded the specification limits, but were reduced upon blending due to often poorer attributes of the petroleum F-76. Although the neat DSH-76 met all the chemical and physical requirements of MIL-DTL-16884L, the data is presented for information purposes only. Neat DSH-76 is not considered a fit for purpose finished fuel for naval applications because it did not meet all FFP requirements.

Table 2. Naval Distillate Fuel Specification Test Results for Batch 1: DSH-76, 50/50 F76/DSH76, 70/30 F76/DSH76, and Petroleum F-76and Petroleum F-76

Test	Parameter	Method	Units	Min	Max	DSH-76 Batch 1	50/50 F76/DSH76 Blend 1	70/30 F76/DSH76 Blend 2	F-76 in Blends 1 and 2
Appearance		D4176	-----	Clear, bright, particle free		Clear & Bright	Clear & Bright	Clear & Bright	Clear & Bright
Demulsification		D1401	minutes		10	2	1	2	3
Density at 15°C		D4052	kg/m ³		876	773	813	829	855
Distillation	10% Recovered	D86	°C	Report		244	233	229	217
	50% Recovered	D86	°C	Report		245	251	258	261
	90 % Recovered	D86	°C		357	245	303	315	316
	End Point	D86	°C		385	255	338	346	343
	Residue		Volume %			1.3	1.6	1.3	1.5
	Loss		Volume %			0.0	0.2	0.2	0.5
	Residue + Loss	D86	Volume %		3.0	1.3	1.8	1.5	2.0
Cloud Point		D5773	°C		-1	-81	-20	-18	-20
Color		D1500	-----		3	1	0.5	1	0.6
Flash Point		D93	°C	60		85	79	77	72
Particulate Contamination		D6217	mg/L		10	0	0	0	0.1
Pour Point		D5949	°C		-6	-75	-30	-27	-30
Viscosity at 40°C		D445	cs	1.7	4.3	2.3	2.6	2.7	2.8
Acid Number, Total		D974	mgKOH/g		0.30	0.01	0.05	0.04	0.04
Ash		D482	Mass %		0.005	0.000	0.000	0.000	0.000
Carbon Residue on 10% Bottoms		D524	Mass %		0.20	0.03	0.12	0.19	0.18
Copper Strip Corrosion at 100 °C		D130	-----		1	1a	1a	1a	1a
Hydrogen Content		D7171	Mass %	12.5		14.9	13.9	13.6	13.1
Ignition Quality	Cetane Number	D6890	-----	42		60	56	53	46
Storage Stability, total insolubles		D5304	-----		3.0	0.5	0.6	0.8	1.1
Sulfur, Total	XRF or,	D4294	Mass %		0.30	N/A	0.09	0.12	0.10
	UV Fluorescence	D5453	ppm		3000	0	N/A	N/A	N/A
Trace Metals	Calcium	D7111	ppm		1.0	< 0.1	< 0.1	< 0.1	< 0.1
	Lead	D7111	ppm		0.5	< 0.1	< 0.1	< 0.1	< 0.1
	Potassium	D7111	ppm		1.0	0.1	< 0.1	< 0.1	< 0.1
	Vanadium	D7111	ppm		0.5	< 0.1	< 0.1	< 0.1	< 0.1

Table 3. Naval Distillate Fuel Specification Test Result for Batch 2: DSH-76, 50/50 F76/DSH76, and Petroleum F-76

Test	Parameter	Method	Units	Min	Max	DSH-76 Batch 2	50/50 F76/DSH76 Blend 3	F-76 in Blend 3
Appearance		D4176	-----	Clear, bright, particle free		Clear & Bright	Clear & Bright	Clear & Bright
Demulsification		D1401	minutes		10	2	2	4
Density at 15°C		D4052	kg/m ³		876	777	815.1	857
Distillation	10% Recovered	D86	°C	Report		242	231	214
	50% Recovered	D86	°C	Report		245	249	261
	90 % Recovered	D86	°C		357	245	289	315
	End Point	D86	°C		385	258	337	344
	Residue		Volume %			1.6	1.5	1.6
	Loss		Volume %			0.0	0.1	0.3
	Residue + Loss	D86	Volume %		3.0	1.6	1.6	1.9
Cloud Point		D5773	°C		-1	-82	-28	-22
Color		D1500	-----		3	<0.5	0.5	0.9
Flash Point		D93	°C	60		>85	81	70
Particulate Contamination		D6217	mg/L		10	0	0	2
Pour Point		D5949	°C		-6	<-75	-48	-36
Viscosity at 40°C		D445	cs	1.7	4.3	2.4	2.5	2.7
Acid Number, Total		D974	mgKOH/g		0.30	0.01	0.02	0.03
Ash		D482	Mass %		0.005	0.000	0.000	0.000
Carbon Residue on 10% Bottoms		D524	Mass %		0.20	0.04	0.06	0.11
Copper Strip Corrosion at 100 °C		D130	-----		1	1a	1a	1a
Hydrogen Content		D7171	Mass %	12.5		14.8	13.9	12.9
Ignition Quality	Cetane Number	D6890	-----	42		58	55	47
Storage Stability, total insolubles		D5304	-----		3.0	1.2	0.6	1.1
Sulfur, Total	XRF or,	D4294	Mass %		0.30	N/A	0.04	0.07
	UV Fluorescence	D5453	ppm		3000	1	N/A	N/A
Trace Metals	Calcium	D7111	ppm		1.0	< 0.1	< 0.1	< 0.1
	Lead	D7111	ppm		0.5	< 0.1	< 0.1	< 0.1
	Potassium	D7111	ppm		1.0	< 0.1	< 0.1	< 0.1
	Vanadium	D7111	ppm		0.5	< 0.1	< 0.1	< 0.1

3.3 Fit-for-purpose Level 1 Test Results

Fit-for-purpose testing was performed on neat DSH-76 Batches 1 and 2, blends 1 thru 3, and the petroleum F-76 used in each blend. It should be noted that the same petroleum F-76 was used to make blends 1 and 2, but different petroleum F-76 was used to make blend 3.

Upon blending conventional F-76 with neat DSH, the cetane number of the blended fuel improved over that of the unblended F-76. Neat DSH has a higher cetane than most conventional petroleum fuels. Higher cetane diesel fuels can reduce start times and improve fuel combustion in some compression ignition engines.² Figure 1 shows the cetane number of DSH blends near the historical high for all F-76 procured between 1999-2009. Adding DSH to F-76 will improve the cetane number and may improve diesel engine performance.

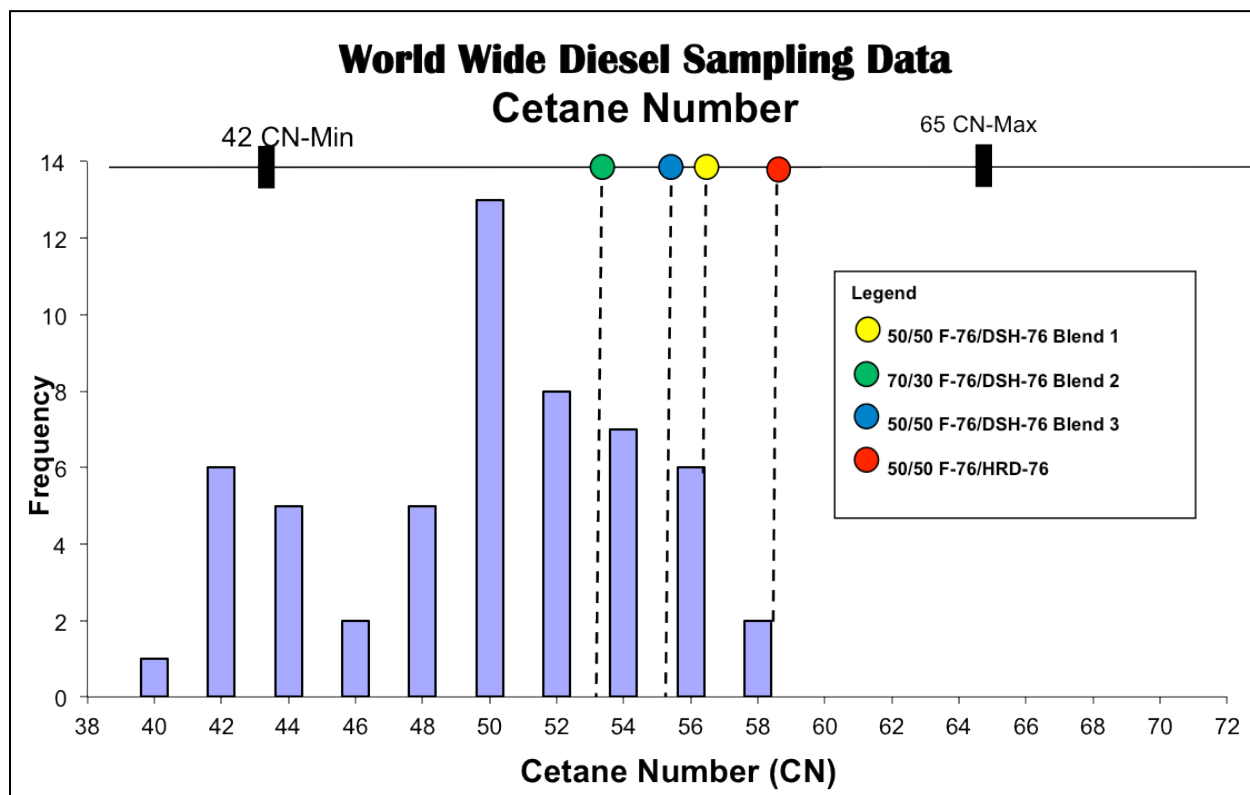


Figure 1: Cetane Number of 50/50 F76/DSH-76 blends 1 and 3 and 70/30 F76/DSH-76 blend 2 compared to 50/50 F-76/HRD-76 and 2009 Worldwide Fuel Survey

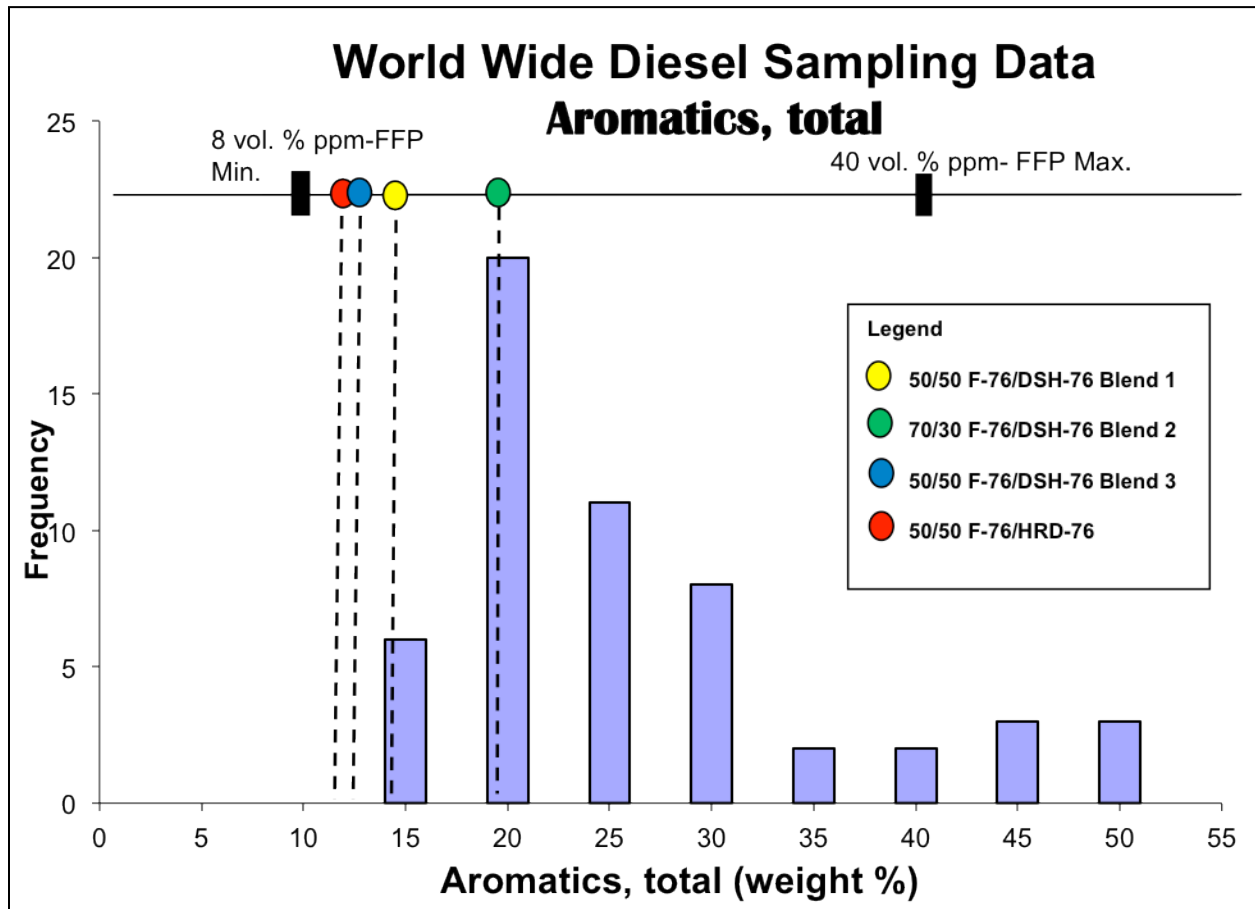


Figure 2: Aromatic content of 50/50 F-76/DSH-76 blends 1 and 3 and 70/30 F-76/DSH-76 blend 2 compared to 50/50 F-76/HRD-76 and 2009 Worldwide Fuel Survey

Aromatics content of the 50/50 and 70/30 DSH blends met the FFP acceptance criteria. Aromatic content can affect the performance of some non-metallic materials such as O-rings and gaskets. Aromatic content is directly related to volumetric heat of combustion, density, and autoignition temperature. Neat DSH-76 does not contain any aromatics but upon blending, the aromatics present in F-76 pass FFP limits. Figure 2 shows the aromatics content of DSH blends and HRD blends along with aromatics content of worldwide diesels sampled in 2010. Although the blends lie near the minimum aromatics limit, extensive testing with HRD blends has verified the FFP aromatics minimum limit. Blending DSH 50/50 with petroleum F-76 increases the aromatic content and passes the FFP acceptance criteria.

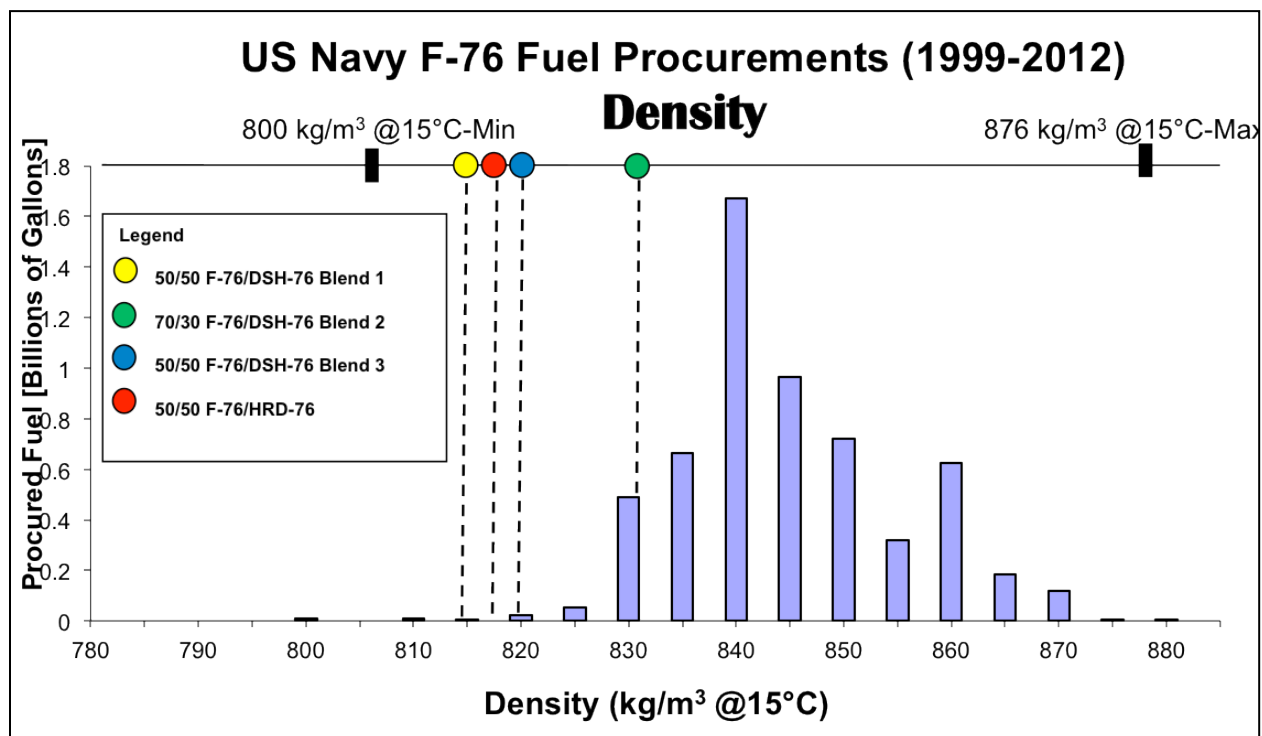


Figure 3. Density of 50/50 F-76/DSH-76 blends 1 and 3 and 70/30 F-76/DSH-76 blend 2 compared to 50/50 F-76/HRD-76 and 1999-2012 US Navy procurement history

As was the case with aromatics, the density of 50/50 F76/DSH76 blends meets the FFP criteria but falls below the historical minimum density of typical petroleum F-76. Figure 3 shows the density distribution of all F-76 procured by the US Navy in the past ten years. The 70/30 DSH blend, 50/50 DSH blends and 50/50 HRD blend are shown in comparison to the petroleum F-76. Extensive ship trials and qualification of HRD blends with similar densities have shown no adverse effects.

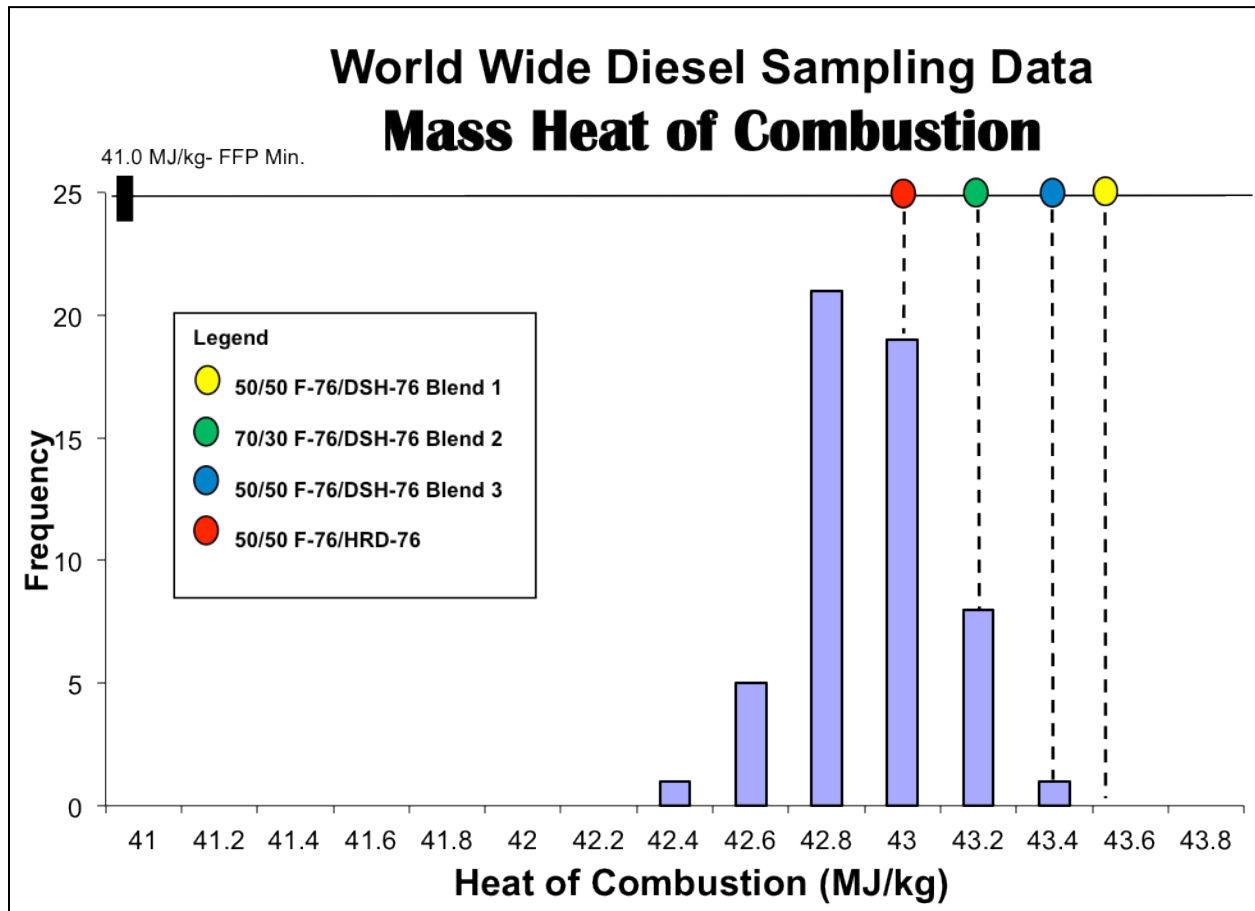


Figure 4. Heat of Combustion (by mass) of 50/50 F76/DSH-76 blends 1 and 3 and 70/30 F-76/DSH-76 blend 2 compared to 50/50 F-76/HRD-76 and 2009 Worldwide Fuel Survey³

Mass heat of combustion for DSH blends were near the highest levels of mass heat of combustion for diesel fuels measured in the 2010 world fuel survey³. Neat DSH had a mass heat of combustion which was even higher, but blending with F-76 lowered this value to within conventional diesel fuel. Volumetric heat of combustion, shown in Figure 5, was lower than that of conventional diesel fuels, but within fit for purpose limits. The lower volumetric heat of combustion was attributed to the density of DSH being lower than typical petroleum diesel. HRD also showed a similar trend with respect to heat of combustion. Neat HRD also had a high mass heat of combustion but lower volumetric heat of combustion due to its lower density. However, despite the slightly lower than typical heat of combustion, all shipboard trials with HRD to date have not shown any negative impact to operational performance^{4,5,6,7,8}.

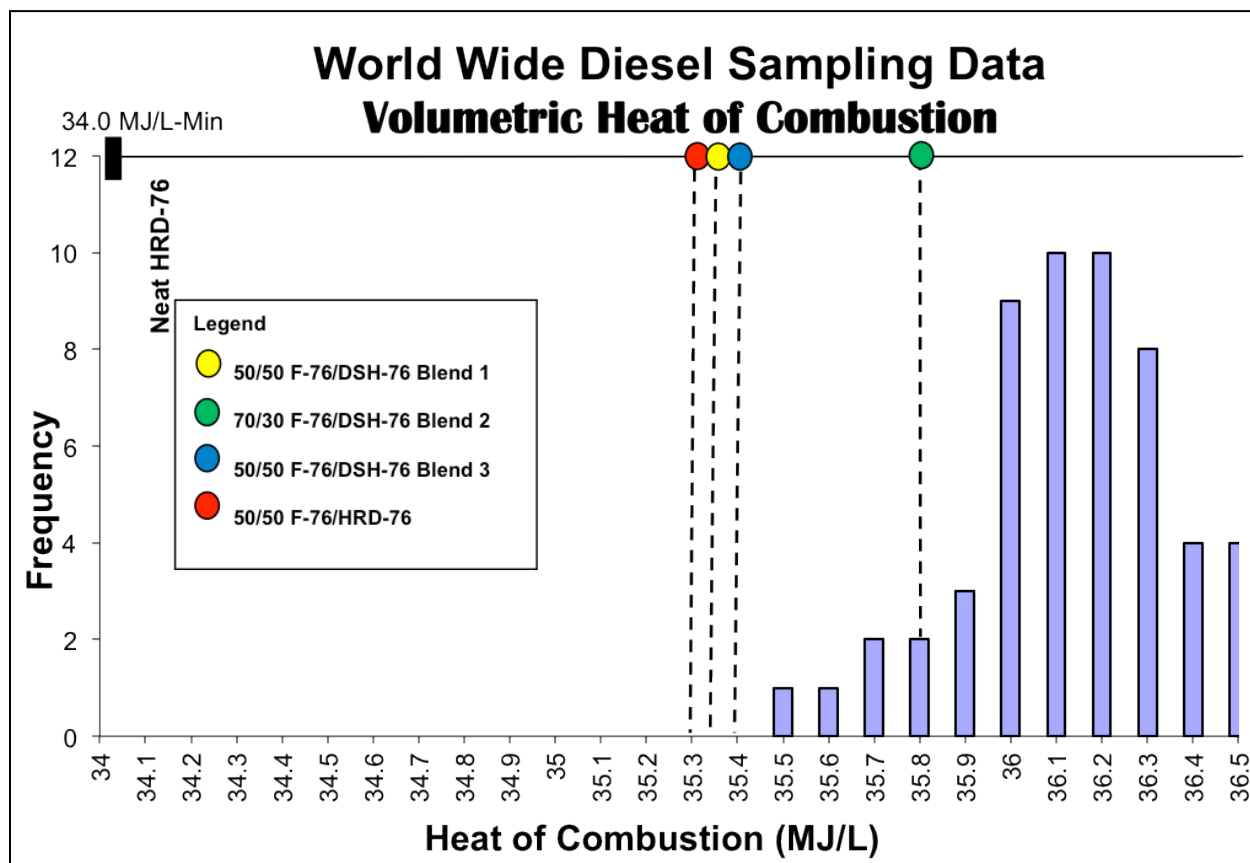


Figure 5. Heat of Combustion (by volume) of 50/50 F76/DSH-76 blend 1 and 3 and 70/30 F76/DSH-76 blend 2 compared to 50/50 F-76/HRD-76 and 2009 Worldwide Fuel Survey³

Blends of DSH-76 with petroleum F-76, all properties met the FFP acceptance criteria with the exception of nitrogen content, thermal stability and autoignition temperature. Nitrogen content and thermal stability of the neat DSH-76 met the FFP acceptance criteria. The F76/DSH blends did not pass the nitrogen content and thermal stability requirements because the petroleum F-76 used in the blends did not pass the FFP acceptance criteria for these two properties. The 50/50 F76/DSH blends had an autoignition temperature of 223°C and 225°C which are near the FFP limit of 226.7°C, but do not pass the acceptance criteria. Further review by the fire safety experts may be required for any potential fire safety impacts.

Neat DSH-76 Batch 1 did not pass the FFP limits for storage stability. Antioxidants may not have been initially added to the fuel, which would explain the high amount of peroxides initially present in the fuel. Antioxidants were added to Batch 2 of DSH-76 and this batch met the storage stability requirements. Antioxidants will be required in DSH-76 in order to prevent peroxidation and gum formation.

Blends 1 and 2 of F76/DSH-76 passed lubricity testing, but blend 3 did not pass lubricity testing. A lubricity additive was added to blend 3 at 100 ppm in order to achieve an acceptable HFRR lubricity of 450 µm (data not shown on Table 5).

One of the most prominent effects having a single molecule compound is the boiling point distribution. Petroleum fuels and other alternative fuels are comprised of a mixture of compounds with carbon numbers between 10 and 22. DSH-76 has nearly all iso-alkane of carbon number 15. The resulting boiling point curve for DSH is nearly “flat”, as a pure compound will only have a single boiling point. Figure 6 shows the distillation curve of neat DSH-76, blends of DSH-76 and F-76. Additionally the distillation minimums from worldwide fuel survey (a “snap shot in time” of fuel property data) and 1999-2012 PQIS data (historical experience of all F-76 procured for US Navy use) were plotted to show current range of diesel fuel distillation curves. After blending, 50/50 F-76/DSH-76 had a distillation curve similar to F-76. In fact, some F-76’s from the PQIS data base show the Navy fleet has received F-76 fuels with distillation temperatures that was less than the DSH blend.

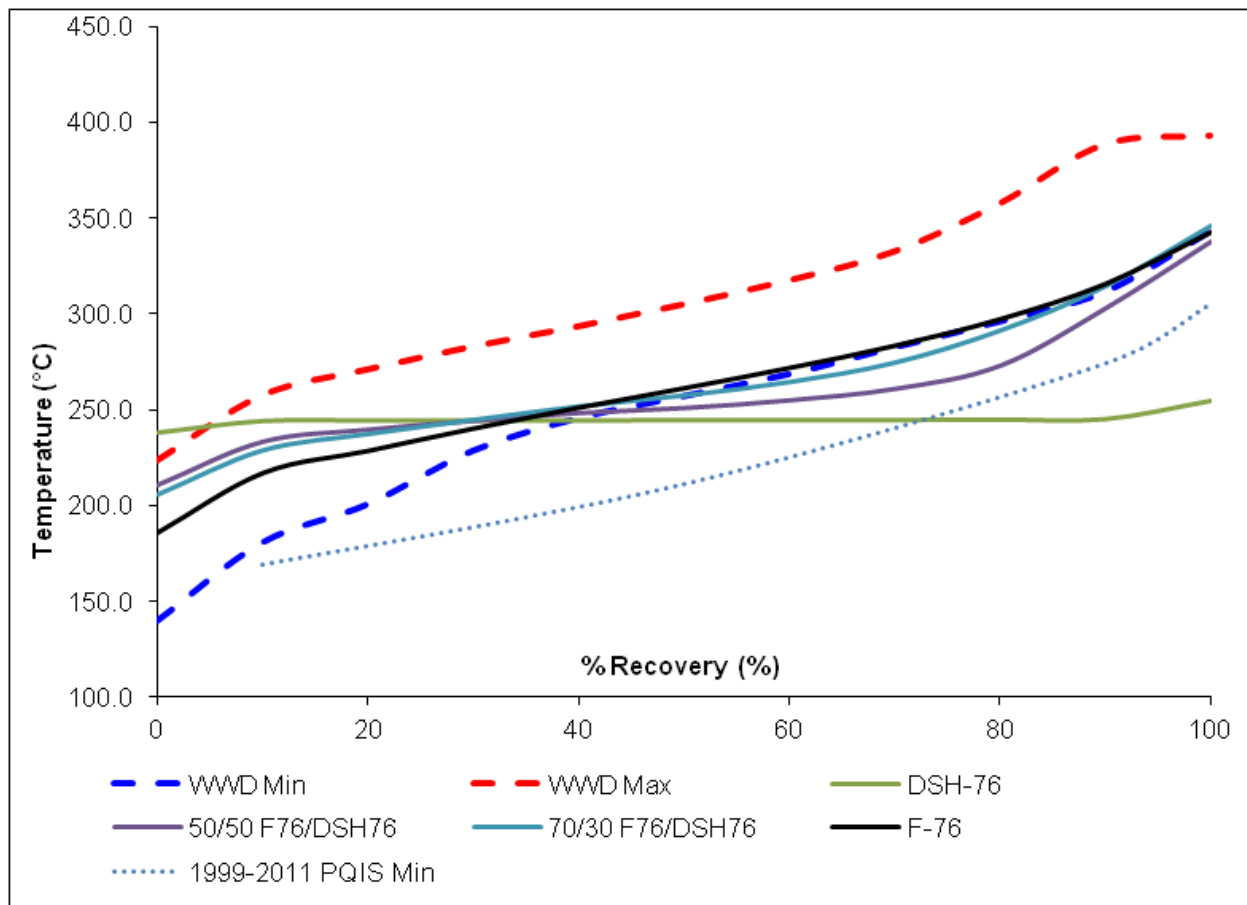


Figure 6. World Wide Diesel Sampling Data Boling Point Curve

Table 4. Fit-for-purpose Level I Test Results Batch 1: DSH-76, 50/50 F76/DSH-76, 70/30 F76/DSH-76, and Petroleum F-76

Characteristic	Parameter	Test Method	Units	Acceptance Criteria		100% DSH-76	50/50 F-76/DSH-76	70/30 F76/DSH76	F-76
				min	max				
Aromatics	Total Aromatics	ASTM D6379, D2425	vol %	8	40	0	14	19	26
Autoignition Temperature	Autoignition Temperature	ASTM E659	Celsius	226.7	--	199	223	226	233
Cetane Number, Derived		ASTM D6890	--	42	67	60	56	53	46
Density	Density @ 15 C	ASTM D4052	kg/m ³	800	876	773	813	829	855
	Density @ 25 C		kg/m ³	793	855	766	806	822	848
Distillation	Distillation IBP	ASTM D86	Celsius	Report Only		238	211	206	186
	Distillation 20% Point		Celsius			244	240	238	229
	Distillation 30% Point		Celsius			244	244	245	240
	Distillation 40% Point		Celsius			244	248	252	251
	Distillation 50% Point		Celsius			245	251	258	261
	Distillation 60% Point		Celsius			245	255	265	272
	Distillation 70% Point		Celsius			245	261	275	284
	Distillation 80% Point		Celsius			245	273	292	298
Electrical Conductivity		ASTM D2624	pS/m	Report Only		0	3	4	8
Existent Peroxides		ASTM D3703	ppm	--	8	0	0	0	0
Filtration Time		MIL-DTL-5624U Appendix A	min/L	--	30	NR	NR	NR	11
Fuel & Additive Compatibility		ASTM D4054	--	No visual sediment formation		PASS	PASS	PASS	PASS
Heating Value	Heating Value (by mass)	ASTM D4809	MJ/kg	43.0	--	43.9	43.5	43.2	42.7
	Heating Value (by volume)		MJ/L	34.0	--	34.0	35.3	35.8	36.5
Hydrocarbon Composition Analysis	Paraffins	GC/MS In-house method		No unusual contaminants found (i.e. not normally present in petroleum diesel fuel)		99.9	74.0	79.6	75.9
	Mono-cycloparaffins					0.0	6.8	3.3	4.8
	Di-cycloparaffins					0.0	0.5	0.5	0.4
	Tri-cycloparaffins					0.0	0.0	0.0	1.7
	Alkyl benzenes					0.0	6.2	4.7	6.4
	Indans & Tetralins					0.0	2.8	2.9	1.5
	Indenes					0.0	0.0	0.0	0.0
	Naphthalene					0.0	0.0	0.0	0.0
	Naphthalenes					0.0	0.0	0.0	0.8
	Acenaphthenes					0.0	0.0	0.0	0.0
	Acenaphthylenes					0.0	0.0	0.0	0.0
	Tri-cyclic aromatics					0.0	0.0	0.0	0
Interfacial Tension		ASTM D1331, D971	dyne/cm	20	--	29	23	28	27
Lube Oil Compatibility		NAVSEA In-house	--	visual sediment format		PASS	PASS	PASS	PASS
Lubricity (BOCLE)		ASTM D5001	um	--	650	642	595	579	574
Lubricity (HFRR)		ASTM D6079	um	--	460	560	460	430	390
Nitrogen Content		ASTM D4629	ppm	--	100	2	99	132	248
Smoke Point		ASTM D1322	mm	10	--	44	25	22	14
Storage Stability (Peroxides)	24 hr	NAVAIR PSEF-TM-FLT-055-007	ppm	--	Report	46	3	2	2
	48 hr				Report	225	3	2	2
	72 hr				16	860	3	3	7
Surface Tension @ 20 C		ASTM D1331	mN/m	23	--	26	27	30	29
Thermal Stability (gas turbine)		ASTM D3241	Celsius	220	--	>340	215	215	195
Trace Metals	Trace Metals - Iron	ASTM D7111	ppm	--	0.5 (combined total)	<0.1	< 0.1	< 0.1	< 0.1
	Trace Metals - Lithium					<0.1	< 0.1	< 0.1	< 0.1
	Trace Metals - Magnesium					<0.1	< 0.1	< 0.1	< 0.1
	Trace Metals - Manganese					<0.1	< 0.1	< 0.1	< 0.1
	Trace Metals - Nickel					<0.1	0.1	< 0.1	0.3
	Trace Metals - Zinc					<0.1	< 0.1	< 0.1	<0.1
Viscosity	Viscosity @ 0 C	ASTM D445	cSt	5.0	18.0	6.4	6.7	7.9	8.1
	Viscosity @ 15 C		cSt	3.0	10.0	4.1	4.5	4.6	5.0
Water Solubility @ 30 C		ASTM D6304 modified	ppm	0	150	91	98	97	115

*Values highlighted in red denote properties that do not meet procurement specification

Table 5. Fit-for-purpose Level I Test Results Batch 2: DSH-76, 50/50 F-76/DSH-76, and Petroleum F-76

Characteristic	Parameter	Test Method	Units	Acceptance Criteria		DSH-76 Batch 2	50/50 F-76/DSH-76 Blend 3	F-76 in Blend 3
				min	max			
Aromatics	Total Aromatics	ASTM D6379, D2425	vol %	8	40	0	12	22
Autoignition Temperature	Autoignition Temperature	ASTM E659	Celsius	226.7	--	200	225	234
Cetane Number, Derived		ASTM D6890	--	42	67	58	55	47
Density	Density @ 15 C	ASTM D4052	kg/m ³	800	876	777	815	857
	Density @ 25 C		kg/m ³	793	855	766	808	850
Distillation	Distillation IBP	ASTM D86	Celsius	Report Only		236	211	185
	Distillation 20% Point		Celsius			245	238	228
	Distillation 30% Point		Celsius			245	242	240
	Distillation 40% Point		Celsius			245	246	251
	Distillation 50% Point		Celsius			245	249	261
	Distillation 60% Point		Celsius			245	252	271
	Distillation 70% Point		Celsius			245	257	284
	Distillation 80% Point		Celsius			245	266	297
Electrical Conductivity		ASTM D2624	pS/m	Report Only		19	16	8
Existent Peroxides		ASTM D3703	ppm	--	8	0	0	0
Filtration Time		MIL-DTL-5624U Appendix A	min/L	--	30	12	10	15
Fuel & Additive Compatibility		ASTM D4054	--	No visual sediment formation		PASS	PASS	PASS
Heating Value	Heating Value (by mass)	ASTM D4809	MJ/kg	43.0	--	43.8	43.4	42.8
	Heating Value (by volume)		MJ/L	34.0	--	34.1	35.4	36.7
Hydrocarbon Composition Analysis	Paraffins	GC/MS In-house method	vol %	No unusual contaminants found (i.e. not normally present in petroleum diesel fuel)		99.9	74.0	75.9
	Mono-cycloparaffins					0.0	6.8	4.8
	Di-cycloparaffins					0.0	0.5	0.4
	Tri-cycloparaffins					0.0	0.0	1.7
	Alkyl benzenes					0.0	6.2	6.4
	Indans & Tetralins					0.0	2.8	1.5
	Indenes					0.0	0.0	0.0
	Naphthalene					0.0	0.0	0.0
	Naphthalenes					0.0	0.0	0.8
	Acenaphthenes					0.0	0.0	0.0
	Acenaphthylenes					0.0	0.0	0.0
	Tri-cyclic aromatics					0.0	0.0	0
Interfacial Tension		ASTM D1331, D971	dyne/cm	20	--	30	30	25
Lube Oil Compatibility		NAVSEA In-house	--	No visual sediment formation		PASS	PASS	PASS
Lubricity (BOCLE)		ASTM D5001	um	--	650	610	580	580
Lubricity (HFRR)		ASTM D6079	um	--	460	540	490	480
Nitrogen Content		ASTM D4629	ppm	--	100	1	112	246
Smoke Point		ASTM D1322	mm	10	--	42	25	15
Storage Stability (Peroxides)	24 hr	NAVAIR PSEF-TM-FLT-055-007	ppm	--	Report	0	1	2
	48 hr				Report	1	4	4
	72 hr				16	0.68	4	4
Surface Tension @ 20 C		ASTM D1331	mN/m	23	--	26	27	29
Thermal Stability (gas turbine)		ASTM D3241	Celsius	220	--	340	210	200
Trace Metals	Trace Metals - Iron	ASTM D7111	ppm	--	0.5 (combined total)	< 0.1	< 0.1	< 0.1
	Trace Metals - Lithium	ASTM D7111				< 0.1	< 0.1	< 0.1
	Trace Metals - Magnesium	ASTM D7111				< 0.1	< 0.1	< 0.1
	Trace Metals - Manganese	ASTM D7111				< 0.1	< 0.1	< 0.1
	Trace Metals - Nickel	ASTM D7111				< 0.1	< 0.1	< 0.1
	Trace Metals - Zinc	ASTM D7111				< 0.1	< 0.1	< 0.1
Viscosity	Viscosity @ 0 C	ASTM D445	cSt	5.0	18.0	6.7	7.1	7.8
	Viscosity @ 15 C	ASTM D445	cSt	3.0	10.0	4.3	4.5	4.9
Water Solubility @ 30 C		ASTM D6304 modified	ppm	0	150	68	60	77

*Values highlighted in red denote properties that do not meet procurement specification

3.4 Chemical Compositional Analysis

As part of the FFP, the chemical compositional profile of neat DSH-76 was determined with the GC-MS. The GC-MS identifies and classifies the various chemical compounds present in the fuel. These results are represented in Figure 7 and show that DSH-76 is composed of >98% farnesane, a 15 carbon number iso-paraffinic hydrocarbon. A few minor components side products of farnesane, a 15 carbon number iso-paraffinic alcohol, and a cyclic isomer of farnesane were also present at less than 1%. The trace impurities had no impact on the Fit for Purpose properties shown in Table 4 and 5. All compounds identified in the neat DSH-76 were of similar composition and molecular weight to hydrocarbons normally present in petroleum F-76 diesel fuels. When blended with conventional F-76, a broad distribution of paraffinic and aromatic molecules are present with farnesane as the predominate molecule.

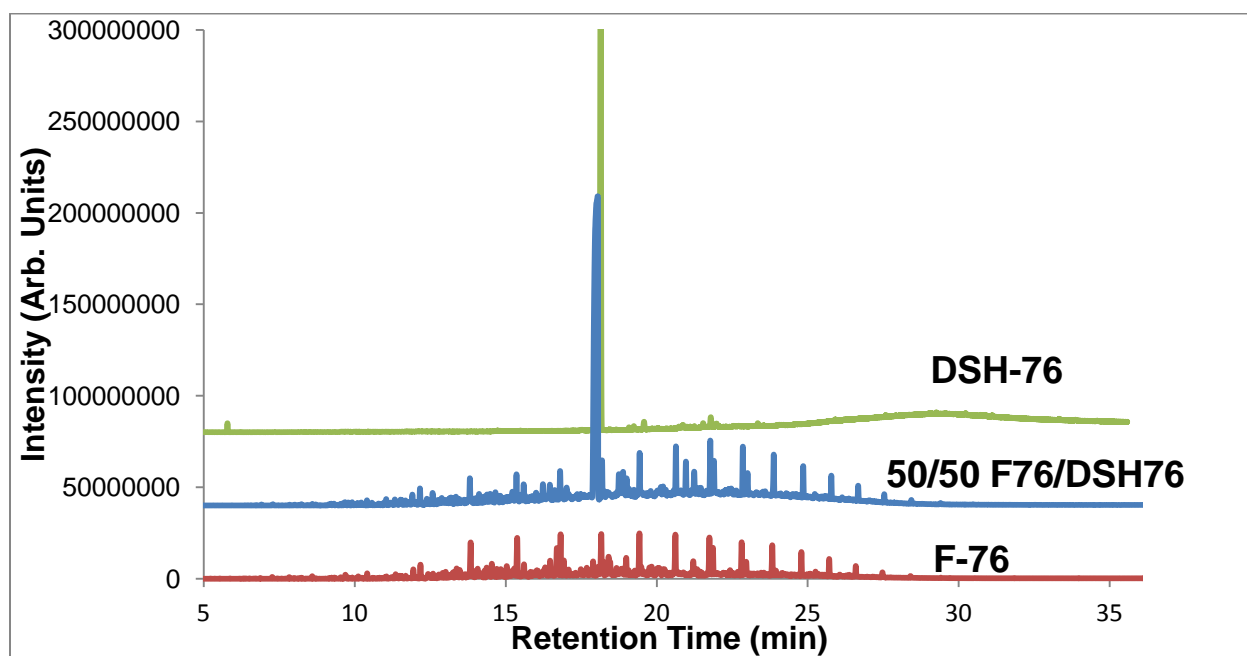


Figure 7. GC-MS of Neat DSH-76, 50/50 F76/DSH76, and F-76

4.0 CONCLUSIONS

Two distinct batches of DSH-76 derived from fermented sugars were blended with petroleum F-76 and examined against MIL-DTL-16884 specifications and Fit-For Purpose Level I acceptance criteria. 70/30 and 50/50 blends of F76/DSH-76 showed chemical and physical properties that were as good as or better than petroleum F-76. Both 70/30 and 50/50 F76/DSH-76 blends met all MIL-DTL-16884 specifications criteria. The distillation profile for 50/50 F76/DSH-76 did not fall outside the range of experience with F-76. 50/50 F76/DSH-76 blends met all FFP criteria, but its autoignition temperature did not pass the acceptance criteria. Further review by the fire safety experts may be required for any potential fire safety impacts.

5.0 RECOMMENDATIONS

It is recommended that 50%/50% petroleum F-76/DSH-76 blends continue qualification testing.

6.0 REFERENCES

- ¹ Turgeon R.T., Morris, R., Williams, S.A, Kamin, R.A, Mearns, D.F.; NF&LCFT 441/12-005 Report "F-76 Alternative fuel Source Qualification-Fit for Purpose Requirements", 30 April 2012.
- ² Bacha, J., Freel, J., Gibbs, A., Hemighaus, G. et. al. "Diesel Fuel Technical Review." Chevron 2007.
- ³ Turgeon R.T., Williams, S.A, Kamin, R.A, Mearns, D.F.; NF&LCFT Report 441/11-003 "Worldwide Marine Diesel Fuel Survey Report" 30 March 2011.
- ⁴ Bautista, J. Q., Sadowski, T.J. Test Report for RCB-X Alternative Fuel Calm Water Powering Trials. Nov 2010. NSWCCD-23-TM-2010/39
- ⁵ 7MRX0601 Alternative Fuels Demonstration Calm-water Propulsion Trials. July 2010. Enclosure to document number 9583 235/3
- ⁶ Pineiro, I. Self Defense Test Ship (SDTS) Alternative Fuel Test Report. February 2012. Document 9234 934/058
- ⁷ Canilang, B., Diamond, P. SLEP LCAC Alternative Fuels Test Report. January 2012. Document number 9234 935/048
- ⁸ Fuel Systems Questionnaire for USS Ford's Trial with 50/50 F76/HRD76

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APPENDIX A

Procurement Specification for Direct Sugar to Hydrocarbon Diesel (DSH-76)

Materials. Direct Sugar to Hydrocarbon Diesel (DSH-76) fuel supplied under this procurement shall consist predominately of an iso-paraffinic molecule (farnesane) and shall be produced solely from sugar derived from biomass.

Properties	ASTM Number	Min	Max
Flash Point, °C	D93	60	
Density @15°C, kg/L	D1298	0.772	0.800
Total Water, ppm	D6304		200
Particulate, mg/l	D6217		1.0
Kinematic Viscosity @40°C, mm ² /s	D445	1.7	4.3
Cetane Number or Cetane Index	D613 D976	42 43	80 80
Distillation IBP, °C 10% (T10), °C 50% (T50), °C 90% (T90), °C FBP, °C Residue+Loss, vol% T50-T10, °C T90-T10, °C	D86	Report 191 Report 230 235 Report Report	290 357 385 3.0
10% Bottoms Carbon Residue, mass %	D524		0.20
Copper Strip Corrosion @ 100°C	D130		No1
Cloud Point, °C	D2500		-1
Hydrogen Content, mass %	D7171	13	
Heating Value, MJ/kg	D4809	43.0	
MSEP Diesel Cap	D7261	85	
Acid Number, mg KOH/g	D974		0.08
Additives Antioxidant ¹ , ppm		17.2	24.0

¹ Antioxidant shall be added as soon as practicable after hydroprocessing or fractionation synthesizing and prior to the product or component being passed into storage to prevent peroxidation and gum formation after manufacture. Antioxidant formulations. The following antioxidant formulations are approved:

- a. 2,6-di-tert-butyl-4-methylphenol
- b. 6-tert-butyl-2,4-dimethylphenol
- c. 2,6-di-tert-butylphenol
- d. 75 percent min-2,6-di-tert-butylphenol, 25 percent max tert-butylphenols and tri-tert-butylphenols
- e. 72 percent min 6-tert-butyl-2,4-dimethylphenol 28 percent max tert-butyl-methylphenols and tert-butyl-dimethylphenols
- f. 55 percent min 2,4-dimethyl-6-tert-butylphenol and 15 percent min 2,6-di-tert-butyl-4-methylphenol and 30 percent max mixed methyl and dimethyl tert-butylphenols

Detailed Process Requirements of Direct Sugar to Hydrocarbon Diesel (DSH-76)

Properties	ASTM Method	Min	Max
Hydrocarbon Composition, mass % Paraffins (normal and iso), mass% Cyclo Paraffins, mass % Total Aromatics, mass %	D2425	84.5	15.0 0.5
Sulfur Content, ppm	D5453		15
Nitrogen Content, ppm	D4629		10
Metals (Ca, Cu, Fe, Mg, Mn, Ni, P, Pb, V, Zn,), ppm	D7111		0.5 total
Alkali Metals and Metalloids (B, Na, K, Si, Li), ppm	D7111		1 total

². All detected metals below the detection limits shall be considered as 0ppb. Only the metals higher than the detection limits count as legitimate values for calculation.

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14. ABSTRACT Direct sugar to hydrocarbon diesel (DSH-76) is an iso-paraffinic single molecule fuel produced from direct fermentation of renewable sugars. This test report summarizes chemical, physical and fit for purpose (FFP) test results of a 70/30 and 50/50 blend of petroleum F-76 and DSH-76. The 70/30 and 50/50 F76/DSH-76 met all specification properties as set forth by MIL-DTL-16884L and FFP criteria as set forth by NAVSEA technical warrant holders, engine OEMs and subject matter experts1. Chemical profiling showed the chemical composition of neat DSH-76 to consist of a C15 iso-paraffinic molecule with very little side products. These test results support the continued qualification of 50/50 F76/DSH-76 for shipboard use by the U.S. Navy.					
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